

I. THE ACTION OF THE GRIGNARD REAGENT  
ON  $\alpha$ -OXIDO KETONES

II. TWO NEW 1,2-DIAROYLCYCLOPENTANES

BY

PETER FOSTER WARFIELD

B.S., Hamilton College, 1940

M.S., University of Illinois, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
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IN CHEMISTRY IN THE GRADUATE SCHOOL OF  
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URBANA, ILLINOIS

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# I. THE ACTION OF THE GRIGNARD REAGENT ON $\alpha$ -OXIDO KETONES

## INTRODUCTION

The attack of the Grignard reagent on  $\alpha$ -oxido ketones has been found to take place at the carbonyl rather than the oxido group.<sup>1</sup> An opportunity was presented to examine this problem from a new viewpoint when it was observed that highly hindered  $\alpha,\beta$ -unsaturated ketones readily formed epoxy derivatives. These substances appeared to provide an opportunity of determining the action of the Grignard reagent on the oxido group of oxido ketones without interference by the carbonyl group.

That such an approach to the problem might prove fruitful was shown by Sperati<sup>2</sup> who treated oxido duryl  $\alpha$ -mesitylvinyl ketone with methylmagnesium iodide and obtained duryl  $\alpha$ -mesitylvinyl ketone, that is, the oxido compound was simply reduced to the corresponding unsaturated ketone.

## EXPERIMENTAL AND DISCUSSION

The oxido compounds studied in this research were prepared from the  $\alpha,\beta$ -unsaturated ketones by treatment with alkaline hydrogen peroxide. The yields were in the neighborhood of 90 per cent and the products were isolated as stable, white crystals. However, oxido mesityl vinyl ketone and oxido benzalacetomesitylene were obtained as clear, yellow oils.

Oxido mesityl  $\alpha$ -mesitylvinyl ketone, oxido  $\alpha,\beta$ -diphenylvinyl mesityl ketone and oxido  $\alpha,\beta$ -diphenylvinyl duryl ketone were converted to the corresponding unsaturated ketones by ethylmagnesium bromide. Mesityl  $\alpha$ -mesitylvinyl ketone was also produced when the corresponding oxido compound was treated with methylmagnesium iodide or phenylmagnesium bromide.

Since the Grignard reagent adds to  $\alpha,\beta$ -unsaturated ketones in the 1,4-manner, the unsaturated ketone cannot be formed until the reaction mixture is decomposed with ice and hydrochloric acid. Attempts to prepare a benzoate or an acetate of the intermediate in the reaction of oxido mesityl  $\alpha$ -mesitylvinyl ketone with methylmagnesium iodide were unsuccessful, but, when the reaction mixture was treated with acetyl chloride, two products were obtained which had the same composition as the oxido compound. The lower-melting isomer melted at 145-146° and has been tentatively identified as mesitoylmesitylacetalde-

hyde. This compound can also be obtained by heating the oxido compound with 18 per cent sulfuric acid. The higher-melting form melted at 215-216° and was obtained when a few crystals of the lower-melting form dissolved in methanol were allowed to stand in the refrigerator for a week.

When oxido mesitalacetomesitylene is treated with ethylmagnesium bromide, the oxido ring is opened and 2-hydroxy-1,3-dimesityl-1-pentanone is formed.

It appears that only those oxido ketones which have no alpha hydrogen atom are reduced to the unsaturated compound.

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## II. TWO NEW 1,2-DIAROYL CYCLOPENTANES

### INTRODUCTION

1,2-Diaroylethylenes and 1,2-diaroylethanes are transformed into 1,4-diaroyl-2,6-diaryl-6-hydroxyfulvenes when treated with a molar equivalent of sodium ethoxide.<sup>1,2</sup> It was easy to postulate a mechanism for the conversion of the ethylenes to the fulvenol, but the mechanism of the conversion of the ethanes to the same fulvenol was more obscure.

It was thought that the most logical mechanism for this reaction would involve a dehydrogenation of the ethane to the ethylene as the primary step. In order to test this hypothesis, 1,2-dimesitylcyclopentane was prepared and its reactions were studied.

### EXPERIMENTAL AND DISCUSSION

Thionyl chloride converted pimelic acid into the acid chloride which was then brominated to give *α,α'*-dibromopimelate. This ester was treated with sodium cyanide in absolute ethanol to give ethyl 1-cyano-1,2-cyclopentanedicarboxylate in yields of about 90 per cent. This method has been used repeatedly in this laboratory.<sup>3</sup> Hydrolysis followed by decarboxylation served to convert the cyano ester into 1,2-cyclopentanedicarboxylic acid which was obtained in the *cis* and *trans* forms. However, the *trans* form was obtained in a very pure state when the hydrolysis was allowed to proceed for ninety hours.

Thionyl chloride converted the *trans* acid to the acid chloride which was treated with mesitylene and aluminum chloride using carbon disulfide as the solvent to give *trans*-1,2-dimesitylcyclopentane in yields of about 50 per cent. Treatment of the acid chloride with aluminum chloride and an excess of benzene gave *trans*-1,2-dibenzoylcyclopentane in yields of about 80 per cent.

Neither of the diketones mentioned above would dissolve in boiling, concentrated sodium hydroxide, and the dibenzoylcyclopentane formed a dioxime, m.p. 140-142°, when treated with hydroxylamine. This evidence substantiated the belief that these compounds did not have the phthalide structure.

When *trans*-1,2-dimesitylcyclopentane was treated with an equivalent amount of sodium ethoxide, orange crystals of a product that melted at 250-251° were obtained. This product had the composition of 1,2-dimesitylcyclopentadiene and decolorized a dilute solution of bromine in carbon tetrachloride, thus showing that sodium ethoxide is capable of acting as a dehydrogenating agent. Consequently, the following mechanism is proposed for the conversion of the 1,2-diaroylethanes to the fulvenols. The ethane is dehydrogenated to the ethylene which then undergoes a Michael reaction followed by a cyclodehydration, an isomerization and an enolization to give the fulvenol.

When *trans*-1,2-dimesitylcyclopentane is treated with ethylmagnesium bromide, two products are obtained. The first has the composition  $C_{25}H_{28}O_3$ , m.p. 179.5-180.5°, and the second has the composition  $C_{22}H_{26}O_2$ , m.p. 145-147°. The structures of these products have not as yet been determined.

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## VITA

The writer was born in Rye, New York on August 4, 1918. He attended the Harvey School, Hawthorne, New York and then the Avon School, Avon, Connecticut, from which he graduated in June, 1935. He entered Hamilton College, Clinton, New York in the fall of 1936 and graduated in June, 1940 with the degree of Bachelor of Science. That fall he entered the Graduate School of the University of Illinois and received the degree of Master of Science in June 1941. He held a University Fellowship for one year and a teaching assistantship in Chemistry from September 1942 to June 1944.





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